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Nanostructured Thin Films Obtained from Fischer Aminocarbene Complexes

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Abstract: The synthesis of four amphiphilic organometallic complexes with the general formula RC = M(CO)5NH(CH2)15CH3, where R is a ferrocenyl 2(a-b) or a phenyl 4(a-b) group as a donor moiety and a Fischer carbene of chromium (0) or tungsten (0) as an acceptor group, are reported. These four push-pull systems formed Langmuir (L) monolayers at the air-water interface, which were characterized by isotherms of surface pressure versus molecular area and compression/expansion cycles (hysteresis curves); Brewster angle microscopic images were also obtained. By using the Langmuir–Blodgett (LB) method, molecular monolayers were transferred onto glass substrates forming Z-type multilayers. LB films were characterized through ultraviolet-visible spectroscopy, atomic force microscopy and X-ray diffraction techniques. Results indicated that films obtained from 2b complex [(Ferrocenyl)(hexadecylamine)methylidene] pentacarbonyl tungsten (0) are the most stable and homogeneous; due to their properties, these materials may be incorporated into organic electronic devices.

Keywords: LB films; ferrocene derivatives; carbene complexes; nanostructures; thin films

1. Introduction

During the last decade, considerable efforts have been carried out to obtain materials for electronic and optoelectronic applications, which led to molecular electronics, a new, important, and interdisciplinary field of research [1]. Although most research has been devoted to inorganic materials, few studies about organic and organometallic derivatives may also be found. In this sense, organometallic entities have attracted considerable attention due to their plausible electron transfer processes [2]. Particularly, those containing ferrocene (Fc) have emerged as an important π-conjugated donor group in the construction of “push-pull” systems, which possess charge-transfer excited states [3–5]. The main characteristics of these ferrocenyl derivatives can be listed as follows: quasi-reversible oxidation, chemical stability, high stability under light irradiation, and reductive quenching of excited molecules [6], being implicated in electrochemical and redox systems [7,8], luminescent, and photochromic systems [9].
Conductive devices [10], biosensors [11], and chemosensors [12], among others. A promising scaffold to evaluate electronic transport through conjugated frameworks are the Fischer carbene complexes, which include studies on electron transfer processes involving electronic interactions between electron-donor (D) and electron-acceptor (A) groups [13–18].

In a previous work, ferrocenyl Fischer carbenes were incorporated in thin films by thermal evaporation processes displaying a semiconductor character. In that study we found that the thin morphology strongly depended on the metallic ion in the molecular structure; thus, the materials were amorphous or poorly crystalline and, unfortunately, not all the compounds sublimate easily [19]. In order to analyze and improve the properties of these materials, in this work we report the incorporation of Fischer aminocarbenes into nanostructured LB films [20,21]. The title aminocarbenes were designed as push-pull systems, in which the ferrocenyl or phenyl fragments can act as electron-donor groups, and the corresponding Fischer carbene (Cr or W) moieties can function as strong electron-acceptor groups. The introduction of a long alkyl chain would allow the amphiphilic character necessary to make them suitable to the LB technique [22,23]. Related studies in which ferrocenyl compounds were used as precursors of LB films have found different applications in the area of materials with magnetic [24] and redox [25] properties.

The electrophilic character of the carbenic carbon in Fischer complexes facilitates the attack by nucleophiles such as primary amines. As a consequence of the electrophilic character on carbenic carbon, α-anions were easily generated upon treatment of alkyl carbene complexes with bases [26–28]. Applying this efficient strategy, we synthesized four Fischer aminocarbenes’ amphiphilic character under a push-pull architecture. The preparation of L monolayers and non-centrosymmetric Z-type LB multilayers and the subsequent mono- and multilayer LB-deposition onto glass substrates were also reported. The LB films were characterized by ultraviolet-visible (UV-VIS) spectroscopy, atomic force microscopy (AFM), and X-ray diffraction (XRD). The stability and morphology of these films were studied through combined isotherms, i.e., surface pressure (π) versus molecular area (A), compression–expansion cycles (hysteresis), and Brewster angle microscopy (BAM). The monolayers based on ferrocenyl aminocarbone exhibited more stability in hysteresis curves than the monolayers of phenyl aminocarbone derivatives.

2. Results and Discussion

2.1. Synthesis of Organometallic Precursors

The ferrocenyl (2a-b) and phenyl (4a-b) hexadecylamino carbene Fischer complexes were synthesized in good yields through an aminolysis reaction (with hexadecylamine) of the corresponding ethoxy ferrocenyl (1a-b) and ethoxy phenyl (3a-b) Fischer carbene complexes, respectively [29] (Scheme 1).

Scheme 1. Synthesis of Fischer aminocarbenes of ferrocenyl 2(a-b) and phenyl 4(a-b) complexes.
The obtaining of Fischer aminocarbenes \(2(a-b)\) and \(4(a-b)\) were confirmed by solution NMR spectra (\(^1\)H and \(^{13}\)C), which showed the characteristic signals for these complexes. Particularly, for complexes \(2(a-b)\), we observe the only presence of \(Z\)-isomers. This behavior is presumably due to the bulkiness of the Fc residue, which has a steric repulsion with the side-chain, as observed in other ferrocenyl amino carbenes analogues [30]. In the case of \(4(a-b)\) complexes, they exist as mixtures of \(Z\) and \(E\)-isomers with regard to the partial C-N double bound, being the isomer \(E\) the main specie, in accordance with the literature [31].

In the \(^{13}\)C-NMR spectra, the signal for carbenic carbon appeared around \(\delta = 270 \text{ ppm (2a)}\) and \(281 \text{ ppm (4a)}\) for chromium complexes. For tungsten series, these signals are shifted at \(249 \text{ ppm (2b)}\) and \(258 \text{ ppm (4b)}\). In the region between \(\delta = 223–199 \text{ ppm}\), we can observe the signals due to M–CO. Through infrared spectra, the four complexes displayed the typical M–CO bands around \(2000 \text{ cm}^{-1}\) and a fine band around \(3300 \text{ cm}^{-1}\) assigned to the N–H group. The observed peaks from mass spectrometry were in accordance with the expected molecular ions [(M\(^+\))] for all the complexes.

The UV-VIS spectra of \(2b\) showed three well-defined absorptions bands (which depend on the nature of the substituent attached to the carbene carbon atom). These bands have been identified as a spin-forbidden metal-ligand charge transfer (MLCT) band in the range between 450 and 500 nm, a moderately intense ligand field (LF) band at 387 nm, and an additional, less-intense LF band at 347 nm [3,15,32]. Compared with similar ferrocenyl derivatives, the observed bands in \(2b\) appeared at shorter wavelengths [3,32]. In a similar manner, the Fischer aminocarbone complex \(4b\) displayed three bands at 245 nm, 343 nm, and 370 nm. From this results, it is evident that the MLCT band of ferrocene derivative \(2b\) is slightly red-shifted compared to the phenyl derivative \(4b\) (\(\Delta \lambda = 17 \text{ nm}\)). These results confirmed the \(\pi\)-donor character of the ferrocene fragment [3,15,33]. In both cases, the presence of the amino group [\(\text{NH(CH}_2\text{)}\text{3CH}_3\)] provoked a blue-shifted absorption of the MLCT and LF transitions, similarly to other Fischer-type carbene complexes [34,35]. A comparison of electronic absorption spectra for \(2b\) and \(4b\) complexes is shown in Figure 1. The data revealed that the MLCT and LF bands have a remarkable \(\pi-\pi^*\) character.

![Figure 1. UV–VIS spectra of: (a) \(2b\) and (b) \(4b\) aminocarbone complexes in CHCl\(_3\) solution.](image)

2.2. Langmuir Monolayer Surface

The Fischer aminocarbone complexes, \(2(a-b)\) and \(4(a-b)\), were able to form L monolayers at the air-water interface. These monolayers were prepared and characterized by measuring the isotherm of surface pressure versus molecular area \((\pi / A)\) and BAM observations. The L monolayers of \(2b\) and \(4b\) were also characterized by hysteresis plots.

2.2.1. Langmuir Monolayers of \(2a\) and \(4a\) Complexes, with Chromium as Transition Metal

Langmuir Isotherm for the \(2a\) Complex

Langmuir films for the ferrocenyl aminocarbene \(2a\) complex (M = Cr) were prepared; the isotherm, which was recorded at 25 °C, is shown in Figure 2. A phase transition, at a surface pressure around 7 mN·m\(^{-1}\) with a molecular area 32.0 ± 2 Å\(^2\), was observed—\textit{in situ}—by BAM images. Additionally,
this plot shows that collapse begins with the formation of a short plateau at a surface pressure around 9 mN·m⁻¹.

**Figure 2.** Surface pressure vs. area isotherm of ferrocenyl aminocarbene complex 2a, M = Cr.

BAM images, which are shown in Figure 3, confirm the formation of L film of the 2a compound. When the surface pressure increases, bands with molecules following the water waves on the surface were observed (see Figure 3a,b). It can be observed the formation of a film with small holes that contain water producing an irregular monolayer, Figure 3c. At a higher surface pressure of 35.0 mN·m⁻¹, a fold of the film was observed, Figure 3d. Some isolated large folds, which appeared between the air-water interface, may be reversible to form a monolayer when the film is expanded [36,37].

**Figure 3.** BAM images (width: 500 µm) of the 2a compound at different surface pressures: (a) 0.5 mN·m⁻¹; (b) 3.0 mN·m⁻¹; (c) 7.0 mN·m⁻¹; and (d) 35.0 mN·m⁻¹.

**Langmuir Isotherm for the 4a Complex**

The isotherm for the phenyl aminocarbene 4a Langmuir film (M = Cr) is shown in Figure 4. The 4a complex exhibited at low surface pressures a molecular rearrangement with the formation of aggregates. Above 9.0 mN·m⁻¹ the collapsed phase was observed, which agrees with the observation of a maximum in the isotherm, which indicates non-equilibrium processes.
Figure 4. Surface pressure vs. area isotherm of phenyl aminocarbene complex 4a, M = Cr.

The 4a film was also characterized through BAM, Figure 5, where a progressive nucleation process can be observed [38,39]. Figure 5a–c showed that the surface of this film became rough as the compression increased, then an inhomogeneous and unstable monolayer appeared.

![BAM Images](image)

Figure 5. BAM images (width: 500 µm) of the 4a compound at different surface pressures: (a) 0.5 mN·m⁻¹; (b) 3.0 mN·m⁻¹; (c) 7.0 mN·m⁻¹; and (d) 14.0 mN·m⁻¹.

In the two-phase coexistence region (where a high-density condensed phase is mixed with a very low-density fluid phase) a variety of agglomerate sizes and shapes can be found producing a film with a poor homogeneity. These agglomerates on the surface depend not only on the chemical structure of the amphiphilic monolayer but also on the decomposition of the complex, which is stable only at low temperatures, between 2 and 4 °C. Finally, the collapse occurred due to the formation of this rough material, Figure 5d. The hysteresis plot could not be obtained since the agglomerates on the surface produced an unstable monolayer.

Results indicated that chromium-carbene compounds, 2a and 4a, produced isotherms which showed well-defined collapses at low surface pressures around 9.0 mN·m⁻¹, with an irregular monolayer formation i.e., low homogeneity and poor stability, because it was not possible to obtain their hysteresis. In the 2a complex there is not reversibility suitable, which was attributed to the “non-return” of the organization molecular formed during compression to their original state after
decompression, and for complex 4a, any reversibility was obtained because several agglomerates were formed during the compression process [20].

2.2.2. Langmuir Monolayers of Aminocarbene 2b and 4b Complexes, with Tungsten as Transition Metal

A second series of complexes with tungsten as transition metal were studied through the LB technique and then compared with those that contain chromium.

Langmuir Isotherm for the 2b Complex

The isotherm of ferrocenyl aminocarbene 2b complex, M = W confirmed the formation of a stable monolayer; no phase transition was observed (see Figure 6). In this figure, it can be observed that collapse begins at a surface pressure around 20.0 mN·m⁻¹; for a surface pressure above 25.0 mN·m⁻¹ the monolayer undergoes the formation of folds.

![Figure 6. Surface pressure vs. molecular area isotherm of ferrocenyl aminocarbene complex 2b, M = W. Inset shows reversibility of two successive compression-expansion cycles.](image)

Hysteresis studies for 2b L monolayer exhibited reversibility on successive compression/decompression cycles, the Figure 6 inset shows in the blue upward direction of compression and red the downward direction corresponding to the decompression. These results indicate the formation of a more stable monolayer for 2b complex than the monolayer for 2a complex, which was assigned to the organization of the molecules, they formed a monolayer during the compression process and the molecules follow the same path returning to their original state after decompression. However, the 2a complex “non-return” to their original state after decompression.

BAM observations, Figure 7, confirmed the formation of 2b ferrocene-derivative film. Indeed, when the surface pressure started to increase slowly large islands throughout the surface were formed Figure 7a,b. When the surface pressure was increased, it could be noticed that molecules begin to form a homogeneous monolayer in the air-water interface. Figure 7c, obtained at 10.0 mN·m⁻¹, the film showed a uniform and homogeneous composition of the monolayer. Finally, at a higher surface pressure, approximately 25.0 mN·m⁻¹, it was possible to observe a transition in which the 2D film goes to a more stable 3D phase [36,37]; therefore, the monolayer collapsed via a folding mechanism, Figure 7d.
Langmuir Isotherm for the 4b Complex

Phenyl aminocarbene 4b complex, M = W, was developed as a L film at the air-water interface. The surface pressure versus molecular area isotherm was recorded under similar conditions than those for 2(a-b) films. BAM observations were also carried out for these films.

From the isotherm, Figure 8, a rearrangement of the molecules at the air-water interface for a surface pressure above 16.0 mN·m⁻¹ was observed. The change in the slope at this value indicated that the collapse of the monolayer begun. Figure 8 inset, shows, in blue, upward direction of compression, and red, the downward direction corresponding to the decompression; the monolayer also exhibited reversibility on successive compression/decompression cycles.

The first two BAM micrographs, Figure 9a,b, show the growth of bands to form an L monolayer. Figure 9c, exhibits a monolayer with some spots or domains. When the compression increased, above 25.0 mN·m⁻¹, the formation of some ridges was observed, Figure 9d.
Isotherms for the tungsten-carbene compounds, 2b and 4b, showed a better formation for both monolayers; it was found that the collapse begins at a surface pressure above 16.0 mN·m⁻¹ a higher value than that for chromium carbene compounds (9.0 mN·m⁻¹). For these two complexes the hysteresis plots showed a better stability of monolayers.

BAM results showed that the 4b L monolayer, M = W, is more homogeneous than that for the 4a complex, M = Cr.

2.3. Langmuir–Blodgett films

Langmuir films were transferred onto solid substrate through the LB method to form Z-type multilayers. Due to their poor homogeneity, 2a and 4a complexes did not form appropriate monolayers, and in this case they were not transferred as LB films. On the other hand, 2b and 4b complexes, both containing tungsten, which exhibited good homogeneity could be transferred onto solid substrates.

The characterization of 2b and 4b LB films were carried out by plotting their absorbance, Figure 10. Insets of Figure 10, show the absorbance as a function of the number of layers. In the first case, for sample 2b at 252 nm, this figure shows a linear increase of absorption at this particular wavelength. This result indicates an efficient transfer of the monolayers onto the glass substrate, as well as the conservation of the molecular arrangement for this complex. However, for 4b compound a stable molecular arrangement was observed only for the film with five layers; above six layers, the linear relationship was lost, Figure 10b.

![Figure 10](image-url)
These results showed that the molecular arrangement of the film which was obtained from the 2b ferrocenyl hexadecylamino Fischer carbene complex showed higher stability and homogeneity than the 4b the phenyl hexadecylamino Fischer carbene complex.

2.4. Atomic Force Microscopy (AFM)

Variations in the morphology and roughness of 2b and 4b LB films, both containing tungsten, were studied by AFM. Results indicated that the 2b monolayer complex is very homogeneous, in good agreement with the results obtained by Brewster angle microscopy during the in situ film formation. The high homogeneity film and low absolute roughness (R_a) for 2b film is observed in Figure 11, where R_a = 2.9 nm.

![Figure 11. AFM micrograph of 2b monolayer film: frontal and 3D views, respectively.](image)

For the 4b complex, the homogeneity decreased, Figure 12. Small domains appeared, probably due to the interactions of the polar heads of this complex, in this case R_a = 3.5 nm. As the number of monolayers increased (e.g., from mono to double-layer) more domains were observed on the surface. Figure 13 shows the formation of small 3D structures on the surface of these films due to the increased number of domains.

![Figure 12. AFM micrographs of 4b monolayer film: frontal and 3D views, respectively.](image)

![Figure 13. AFM micrographs of 4b double-layer film: Frontal and 3D views, respectively.](image)
For the ten layer LB film of 4b complex, the molecular order disappeared due to the formation of a large number of domains and the formation of crests started. The presence of these domains could be the reason why the absorbance of 4b sample, Figure 10b, had a nonlinear behavior. Finally, the morphology studied through AFM showed a well-ordered surface for all the 2b LB films, including the film with ten layers, Figure 14.

![3D AFM micrographs with ten monolayers for 2b and 4b films, respectively.](image)

**Figure 14.** 3D AFM micrographs with ten monolayers for 2b and 4b films, respectively.

### 2.5. Small-Angle X-ray Scattering (SAXS)

SAXS experiments were carried out for 2b LB films, which were deposited onto glass plates. Diffractograms for the ten layers 2b film, after four days and 12 months of deposition, are presented in Figure 15. Results show that this LB film tends to an equilibrium, which was reached only few days after deposition. These data proved the formation of highly ordered and stable LB films similar to those observed for ferrocenyl derivatives [40].

![Small-angle X-ray scattering of a 10-layer Langmuir–Blodgett film of 2b complex: a—four days and b—12 months, after deposition.](image)

**Figure 15.** Small-angle X-ray scattering of a 10-layer Langmuir–Blodgett film of 2b complex: a—four days and b—12 months, after deposition.

### 3. Experimental Section

#### 3.1. Materials

Solvents and precursors used in this study were Aldrich products. Acetone was distilled over calcium chloride; tetrahydrofuran was distilled over sodium and benzophenone under a nitrogen atmosphere. Column chromatography was performed with Merck silica gel (70–230 mesh) and neutral alumina. To analyze their purity, all compounds were characterized by NMR spectroscopy. The $^1$H
and $^{13}$C NMR spectra were recorded on a JEOL Eclipse 300 spectrometer (JEOL Ltd., Tokyo, Japan), using CDCl$_3$ as a solvent and TMS as an internal reference. Chemical shifts are presented in ppm (δ). IR spectra were performed on a Perkin-Elmer 283 B or 1420 spectrometer (PerkinElmer Inc., Waltham, MA, USA). Melting points were obtained on Melt-Temp II equipment (Barnsted Thermolyne, Dubuque, IA, USA). The MS-FAB and MS-EI spectra were obtained with a JEOL SX 102A spectrometer (JEOL Ltd., Tokyo, Japan). The UV–VIS spectra were obtained on a CaryWin 100 Fast-Scan-Varian spectrophotometer (Varian, CA, USA), using fresh solutions of 2a and 2b in CHCl$_3$ spectrophotometric grade. Molar concentrations were prepared in the ranges 8.76 × 10$^{-6}$–4.38 × 10$^{-5}$ mol/L for the 2b complex and 8.81 × 10$^{-6}$ mol/L–5.10 × 10$^{-5}$ mol/L for the 4b complex.

3.2. Synthesis of Organometallic Precursors

3.2.1. Preparation of Fischer Ferrocenyl Hexadecylamino 2(a-b) Complexes

Fischer ethoxy ferroceny carbene 1(a-b) complexes were prepared following a process described in a previous report [29]. Hexadecylamine (1.2 equiv, 2.76 mmol) was added to a solution of 1 (2.3 mmol) in anhydrous ether (10 mL) at room temperature, and then the reaction was stirred overnight. The solvent was evaporated under vacuum and the product was purified through chromatography on alumina using hexane as eluent to obtain an orange solid.

[(Ferrocenylihexadecylamino)methylidene] pentacarbonyl chromium (0) 2a: C$_{32}$H$_{46}$NO$_5$CrFe, orange solid, mp: 80–84 °C, yield: 90%. $^1$H NMR (CDCl$_3$) δ: 9.47 (s, 1H, NH), 4.44 (br s, 4H, Cp$_{subst}$), 4.19 (s, 5H, Cp), 4.04 (m, 2H, NCH$_2$), 1.86 (m, 2H, NCH$_2$CH$_2$), 1.26 (br s, 26H, CH$_2$), 0.88 (br s, 3H, CH$_3$). $^{13}$C NMR (CDCl$_3$) δ: 270.4 (C=Cr), 223.6 (CO), 217.9 (CO), 99.4 (C$_{subst}$), 69.4 (C$_3$), 68.4 (CH, Cp$_{subst}$), 53.0 (NCH$_2$), 32.0 (NCH$_2$CH$_2$), 29.7 (10C, CH$_2$), 27.0 (CH$_2$CH$_2$CH$_3$), 22.8 (CH$_2$CH$_3$), 14.2 (CH$_3$). IR (CHCl$_3$) $\nu_{max}$ cm$^{-1}$: 3306 (N=H), 2050 (CO), 1963(CO), 1898 (CO), 1858 (CO). MS (FAB$^+$) m/z: 573 [(M$^+$ – 2[CO]), 489 [M$^+$ – 5(CO)].

[(Ferrocenylihexadecylamino)methylidene] pentacarbonyl tungsten (0) 2b: C$_{32}$H$_{46}$NO$_5$WFe, orange solid, mp: 74–75 °C, yield: 88%. $^1$H NMR (CDCl$_3$) δ: 9.0 (s, 1H, NH), 4.50 (m, 4H, CH$_2$–N and CH Cp$_{subst}$), 4.18 (br s, 5H, Cp), 3.89 (br s, 2H, CH, Cp$_{subst}$), 1.81 (m, 2H, NCH$_2$CH$_2$), 1.47–1.24 (m, 26H, CH$_2$), 0.86 (br s, 3H, CH$_3$). $^{13}$C NMR (CDCl$_3$) δ: 249.9 (C=Cr), 203.2 (WCO), 198.7 (CO), 97.4 (C$_{ips}$, Cp), 70.9 (CH, Cp$_{subst}$), 69.7 (Cp), 69.6 (CH, Cp$_{subst}$) 55.3 (NCH$_2$), 32.0 (NCH$_2$CH$_2$), 29.8 ((CH)$_2$), 27.0 (CH$_2$CH$_2$CH$_3$), 22.8 (CH$_2$CH$_3$), 14.23 (CH$_3$). IR (CHCl$_3$) $\nu_{max}$ cm$^{-1}$: 3312 (N=H), 2058 (CO), 1961 (CO), 1934 (CO), 1893 (CO), 1864 (CO), 1853 (CO). MS (FAB$^+$) m/z: 761, 760 [M$^+$ + 1], 705 [(M$^+$ – 2[CO]), 677 [(M$^+$ – 3[CO)].

3.2.2. Preparation of Fischer Hexadecylamino Phenyl Carbene 4(a-b) Complexes

Fischer ethoxy phenyl carbene 3(a-b) complexes were prepared following a process described in the literature [26]. Hexadecylamine (2.2 mmol) was added to a solution of 3 (2 mmol) in anhydrous ether (10 mL) at room temperature, and then the reaction was stirred overnight. The solvent was evaporated under vacuum and then the product was purified through chromatography on alumina using hexane as eluent to obtain a stable yellow compound.

[(Phenyl)methylidene]pentacarbonyl chromium (0) 4a: C$_{28}$H$_{39}$NO$_5$Cr, yellow oil, yield: 90% (E/Z, 6:4). $^1$H NMR (CDCl$_3$) δ: 9.0 (s, 1H, NH, isomer E), 8.55 (s, 1H, NH, isomer Z), 8.0 (m, 1H, CH$_{arom}$), 7.58–7.16 (m, CH$_{arom}$) 6.95 (m, 1H, CH$_{meta}$ isomer Z), 6.78 (m, 1H, CH$_{meta}$ isomer E), 4.03 (m, 2H, CH$_2$–N, isomer Z), 3.16 (m, 2H, CH$_2$–N, isomer E), 1.79 (m, 2H, CH$_2$CH$_2$N), 1.26 (m, 26 H, –CH$_2$–), 0.88 (t, 3H, CH$_3$). $^{13}$C NMR (CDCl$_3$) δ: 281.0 (C=Cr, isomer E), 277.7 (C=Cr, isomer Z), 223.8, 223.4 (Cr(CO)), 217.3 (Cr–CO), 155.1 (C$_{ips}$ (isomer Z)), 149.6 (C$_{ips}$ (isomer E)), 128.5, 126.6 and 119.0 (CH$_{arom}$ (isomer E)), 128.7, 128.2 and 120.9 (CH$_{arom}$ (isomer Z)), 53.6 (CH$_2$–N, (isomer Z)), 50.9 (CH$_2$–N, (isomer E)), 31.9, 29.6, 29.2, 26.6, 26.2 and 22.7 (–CH$_2$–), 14.1 (CH$_3$). IR (CHCl$_3$) $\nu_{max}$ cm$^{-1}$: 3355 and 3290 (N=H), 2054, 1974, 1889 (MCO). MS (FAB$^+$) m/z: 493 [(M$^+$ – (CO)], 381 [(M$^+$ – 5(CO)].
[(Phenyl)(hexadecylamine)methylidene] pentacarbonyl tungsten (0) 4b: \( \text{C}_{28}\text{H}_{39}\text{NO}_5\text{W} \), yellow solid, mp: 43–44 °C, yield: 85% (E/Z, 8:1).

\( ^1\text{H NMR (CDCl}_3\) \( \delta \): 9.01 (s, 1H, NH, isomer E), 8.62 (s, 1H, NH, isomer Z), 7.72 (m, 1H, CH\text{arom}), 7.58–7.16 (m, 5H, CH\text{arom}); 7.06–7.02 (m, 1H, CH\text{meta isomer Z}), 6.8–6.78 (m, 1H, CH\text{meta isomer E}).

\( ^{13}\text{C NMR (CDCl}_3\) \( \delta \): 258.0 (C=W), 203.8 (W–CO), 199.1 (W–CO), 155.4 (C\text{ipso}), 131.4, 128.5, 128.2, 126.8, 120.8 (CH\text{arom}), 55.8 (C\text{H}_2–N), 31.9–22.7 (14–CH\text{2–}), 14.2 (CH\text{3}).

IR (CHCl\text{3}) \( \nu_{\text{max}} \) cm\(^{-1}\): 3344 and 3289 (N–H), 2062, 1972, 1895 and 1880 (M–CO). MS (FAB\(^+\)) \( m/z \): 653\([M^+\])], 625\([M^+–(CO)\]), 597 \([M^+–2(CO)\]).

3.3. Preparation of Langmuir Films

The spreading solution was prepared in chloroform with a specific concentration of 1 mg \text{mL}^{-1}. ASTM type 1 ultra-pure water (Millipore-Q system, 18.2 M\(\Omega\)cm) was used for the subphase. Studies on the monolayer were carried out with a KSV 5000 trough system 3 (KSV, Helsinki, Finland), slowly spreading suitable amounts of solution on the water surface with a microsyringe (100 \(\mu\)L). After spreading, the monolayer was maintained for 10 min at room conditions for solvent evaporation. Afterwards, it was symmetrically compressed with a barrier speed of 5 mm min\(^{-1}\). The surface pressure measurement, which was performed according to the Wilhelmy method [20–22], and the isotherm were recorded at 25 °C. Finally, the stability of monolayers was studied through repetitive compression-expansion processes (hysteresis loops) without exceeding the collapse pressure.

Characterization of Langmuir Films through BAM

The quality of the Langmuir films was monitored using a Mini BAM-Plus system from Nanofilm Technology GmbH (Goettingen, Germany). This system is equipped with a 660 nm laser source working at 30 mW. The film quality observations were carried out at the Brewster angle (around 53.15° for an air-water interface) incidence [41,42]. During these experiments, high-resolution images were directly acquired with a built-in CCD camera.

3.4. Preparation of LB Films

The Langmuir monolayers obtained from ferrocene derivatives were transferred onto solid substrates using the Langmuir–Blodgett technique with a vertical lifting method. The transfer ratio value obtained was 1.0 ± 0.1. Films were deposited at 25 °C, using 75 × 75 × 1 mm\(^3\) Pyrex glass plates as substrates. All glass slides were successively treated with a sulfocromic mixture solution, ultrapure water, ethanol (reagent grade, Aldrich, St. Louis, MO, USA) and, finally, chloroform (reagent grade, Aldrich, St Louis, MO, USA). They were subsequently stored under clean and dry conditions until film deposition. Finally, Z-type multilayered structures with \( n = 1, 2, 5, \) and 10 layers were prepared experimentally [21,22] through extraction at a target pressure in the range of 10–12 mN m\(^{-1}\) and a dipping speed of 5 mm min\(^{-1}\), waiting 10 min between successive dipping cycles in order to evaporate the trapped subphase.

Characterization of LB Films

UV-VIS spectra of glass slides with LB films were obtained with a double beam Varian Cary 100 Fast-Scan spectrophotometer (Varian, CA, USA), using a glass slide without LB films as a reference. Unfortunately, the conductive measures of the LB films obtained in this work cannot be obtained because of the limitations of the technique with regard with the thickness of LB films obtained. The diffractograms were obtained with a XRD grazing incidence studies (1°) were carried out with a Rigaku ULTIMA-IV diffractometer Rigaku, Tokio, Japan, 40 kV, 44 mA with CuK\(\alpha\) radiation and AFM images of LB films deposited on glass substrates were acquired using a JEOL-JSPM-4210 atomic force microscope (JEOL Ltd, Akishima-Tokyo, Japan), in tapping mode with a NSC12 rectangular cantilever (\(\mu\)mash \(^{\text{Tm}}\)) and a resonance frequency of 318 kHz (NanoSensors). Scans were performed at room temperature and atmospheric pressure.
4. Conclusions

The synthesis of two series of push-pull organometallic molecules using a Fischer aminocarbene complex \( RC = [M(CO)_5]NH(CH_2)_5CH_3 \), \( [2(a-b)] \) with \( R = Fe \) and \( M = Cr, W \) and \( [4(a-b)] \) with \( R = Ph \) and \( M = Cr, W \) were prepared. For the first group, films of 2b complex from one to ten layers were deposited, and for the second group, films of 4b complex from one to five layers were obtained. The best results in all analyses were found for samples 2b and 4b, since 2a and 4a films were irregular and they formed defects and agglomerates during the Langmuir film formation. For Langmuir films obtained from 2b and 4b complexes, results from BAM showed that the Langmuir monolayer of 2b is very homogeneous in the condensed phase. This behavior could correlate with the spectroscopic evidence of the 2b, which indicate that this amino carbene complex exists solely as a Z-isomer, and this conformation promotes a better molecular arrangement in the Langmuir film.

The UV-VIS spectrum for the 10 layer LB films of 2b showed a better molecular arrangement in comparison to the five layer LB films of 4b. These results also indicated that the monolayers of ferrocenyl aminocarbene complexes (2a, 2b) exhibited more stability than the monolayers of phenyl aminocarbene complexes (4a, 4b).

AFM results for the 2b LB monolayer films showed a homogeneous surface. However, the 4b LB films had a surface with nanodomains and several large solid domains, which produced the loss of structural arrangement as the number of deposited monolayers increased.

AFM data confirmed the results obtained through BAM, since both techniques provided evidence about the molecular arrangement of the films. Results showed that 2b ferrocenyl aminocarbene films exhibited the best stability and homogeneity of all samples, probably due to the larger stability in the electronic interaction between the conjugate bonds of ferrocenyl and the \( \pi \)-bonded carbene carbon-tungsten atoms, which make these nanomaterials suitable for potential electronic applications.

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References